



## DECLARATION

I, Shinichi KAWASAKI of Room 704, 17-34, Miyadacho 2-chome, Takatsuki-shi, Osaka 569-1142 Japan hereby declare that I am conversant with the Japanese language and that I am the translator of the document attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the specification contained in the Priority Document No. JP2002-030515.

Dated this 30th day of October, 2007

A handwritten signature in cursive script, appearing to read "S. Kawasaki", written over a horizontal line.

Shinichi KAWASAKI



2002-030515

(Translation)

[DOCUMENT NAME] Patent Application  
[REFERENCE NUMBER] 2210030019  
[DATE OF SUBMISSION] Heisei 14 (2002), February 7th  
[ADDRESSEE] To: The Commissioner of the Patent Office  
[INTERNATIONAL PATENT CLASSIFICATION] H01M 4/06  
H01M 6/06

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[INDICATION OF OFFICIAL CHARGE]  
[NUMBER IN PRE-PAYMENT REGISTER] 011305  
[AMOUNT PAID] ¥21,000  
[LIST OF DOCUMENTS SUBMITTED]  
[TITLE OF DOCUMENT] Specification 1  
[TITLE OF DOCUMENT] Drawing 1  
[TITLE OF DOCUMENT] Abstract 1  
[NUMBER OF GENERAL POWER OF ATTORNEY] 9809938

2002-030515

(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] ALKALINE BATTERY

[CLAIMS]

[Claim 1] An alkaline battery comprising a positive electrode mixture comprising manganese dioxide and nickel oxyhydroxide as active materials, a negative electrode comprising zinc as an active material, and an alkaline electrolyte, characterized in that the potential of said manganese dioxide is 270 mV or higher (vs. Hg/HgO (40 wt% KOH)).

[Claim 2] The alkaline battery in accordance with claim 1, wherein said positive electrode mixture comprises 20-90 mass% of manganese dioxide and 10-80 mass% of nickel oxyhydroxide.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to an improvement of an alkaline battery that utilizes manganese dioxide and nickel oxyhydroxide as positive electrode active materials.

[0002]

[Prior Art]

Alkaline batteries such as alkaline dry batteries comprise, for example, a positive electrode case which also serves as a positive electrode terminal, a cylindrical

positive electrode mixture which is closely fitted in the positive electrode case, and a gelled negative electrode which is disposed in the center of the positive electrode mixture with a separator interposed therebetween. With a recent increase in load of equipment in which the alkaline batteries are used, there is an increasing demand for alkaline batteries having excellent heavy load discharge performance. Thus, mixing nickel oxyhydroxide into the positive electrode mixture has been examined to improve heavy load discharge performance of batteries (e.g., Japanese Laid-Open Patent Publication No. 2001-015106).

[0003]

[Problem That the Invention Is to Solve]

However, alkaline batteries including manganese dioxide and nickel oxyhydroxide as positive electrode active materials have inferior storage performance to alkaline dry batteries including no nickel oxyhydroxide, and have large self-discharge especially when stored at high temperatures. Thus, after a long-term storage, the heavy load discharge performance thereof is inferior to that of the batteries including no nickel oxyhydroxide. In view of the above problems, an object of the present invention is to provide an alkaline battery capable of retaining heavy load discharge performance even after a long-term storage at high temperatures.

[0004]

[Means for Solving the Problem]

An alkaline battery in accordance with the present invention comprises a positive electrode mixture comprising manganese dioxide and nickel oxyhydroxide as active materials, a negative electrode comprising zinc as an active material, and an alkaline electrolyte, and is characterized in that the potential of the manganese dioxide is 270 mV or higher (vs. Hg/HgO (40wt% KOH)). It is preferable that the positive electrode mixture comprises 20-90 wt% of manganese dioxide and 10-80 wt% of nickel oxyhydroxide.

[0005]

[Mode for Embodying the Invention]

One of the reasons for the self-discharge of alkaline batteries including manganese dioxide and nickel oxyhydroxide as the positive electrode active materials is that difference between potential of manganese dioxide (1) and potential of nickel oxyhydroxide (2) causes formation of a local battery consisting of manganese dioxide and nickel oxyhydroxide in a positive electrode mixture in which an oxidation reduction reaction proceeds.

Normal electrode potential of manganese dioxide = 0.15 V (vs. NHE (25°C)) (1)

Normal electrode potential of nickel oxyhydroxide = 0.49 V (vs. NHE (25°C)) (2)

[0006]

Thus, in order to make such batteries after storage

retain heavy load discharge characteristics, the potential difference between manganese dioxide and nickel oxyhydroxide needs to be reduced to avoid deterioration of nickel oxyhydroxide caused by the formation of the local battery. For this purpose, it is effective to heighten the potential of manganese dioxide and bring it close to the potential of nickel oxyhydroxide.

[0007]

While the potential of nickel oxyhydroxide in an alkaline aqueous solution is 370-410 mV (vs. Hg/HgO (40 wt% KOH)), the potential of commonly used electrolytic manganese dioxide for alkaline batteries is 240-270 mV (vs. Hg/HgO (40 wt% KOH)). When this manganese dioxide is treated with sulfuric acid or the like, lower level manganese oxides on the surfaces of manganese dioxide particles are dissolved, so that manganese dioxide having a potential of 270 mV or higher (vs. Hg/HgO (40 wt% KOH)) is obtained. Use of such manganese dioxide having a potential of 270 mV or higher (vs. Hg/HgO (40 wt% KOH)) makes it possible to reduce the potential difference between the nickel oxyhydroxide and the manganese dioxide, thereby the above-described oxidation reduction reaction is suppressed. If the positive electrode mixture comprises 20-90 wt% of manganese dioxide and 10-80 wt% of nickel oxyhydroxide, discharge characteristics at the initial state and after storage at high temperature become excellent. In particular, if the positive electrode mixture comprises 20-80 wt% of

manganese dioxide and 20-80 wt% of nickel oxyhydroxide, initial discharge characteristic becomes excellent.

[0008]

[Examples]

FIG. 1 is a front view illustrating an alkaline battery according to an example of the present invention, partially in section. This battery is fabricated in the following manner. A positive electrode case 1 is made of steel plated with nickel. A graphite coating film 2 is formed on the inner face of the positive electrode case 1. A plurality of positive electrode mixture pellets 3 in a short cylindrical shape, containing manganese dioxide and nickel oxyhydroxide as main components, are inserted into the positive electrode case 1, which are brought into intimate contact with the inner face of the case 1 by applying pressure again in the case. A separator 4 and an insulating cap 5 are arranged inside the positive electrode mixture pellets 3, and then an electrolyte is injected therein to moisten the separator 4 and the positive electrode mixture pellets 3. As the electrolyte, an aqueous solution of 40 wt% potassium hydroxide is used, for example. After the injection, a gelled negative electrode 6 is filled inside the separator 4. The gelled negative electrode 6 comprises, for example, a gelling agent such as sodium polyacrylate, an alkaline electrolyte and zinc powder as a negative electrode active material. Then, a negative electrode current collector 10 integrated with a



resin sealing plate 7, a bottom plate 8 which also functions as a negative electrode terminal and an insulating washer 9 is inserted into the gelled negative electrode 6. The opening end of the positive electrode case 1 is crimped onto the outer edge of the bottom plate 8 with the outer edge of the resin sealing plate 7 interposed therebetween. Thus, the opening of the positive electrode case 1 is sealed. Then, the outer surface of the positive electrode case 1 is covered with a jacket label 11. Thus, an alkaline battery is completed.

[0009]

(Example 1)

Electrolytic manganese dioxide for alkaline batteries HH-PF manufactured by Tosoh Corporation ( $\text{MnO}_2$  purity: 91% or higher, average particle size obtained by a micro-track method: about 40  $\mu\text{m}$ , pH (JIS): 3.0-4.0, electrode potential:  $255 \pm 15$  mV (vs.  $\text{Hg/HgO}$  (40 wt%  $\text{KOH}$ )) was added to an aqueous solution of 5 wt% sulfuric acid at 60°C to produce a slurry of a concentration of 100 g/l. Subsequently, "the slurry was stirred at 60°C for one hour, and thereafter, electrolytic manganese dioxide was filtered out, washed with water, neutralized with an aqueous solution of sodium hydroxide and then washed again with water." Thereby, electrolytic manganese dioxide with heightened potential was obtained (the above-described step enclosed in "" is regarded as a potential heightening process). Electrode potential of the thus produced manganese dioxide was measured regarding a

mercury/mercury oxide electrode (40 wt% KOH) as a reference electrode. Further, the manganese dioxide, nickel oxyhydroxide and graphite were mixed in a weight ratio of 50:50:5. Further, 1 part by weight of an electrolyte per 100 parts by weight of the active material (manganese dioxide and nickel oxyhydroxide) was added to the above-described mixture, which was stirred with a mixer and granulated to have a certain particle size. The granules thus obtained were pressurized into a hollow cylindrical shape to mold a positive electrode mixture A. The electrolyte used was an aqueous solution of 40 wt% potassium hydroxide. Using the positive electrode mixture A thus obtained, an alkaline battery of AA size as illustrated in FIG. 1 was assembled. This alkaline battery was named as battery A. Batteries at the initial stage and after a 7-day storage at 60°C were continuously discharged at a constant electric power of 1000 mW at 20°C, and discharge duration was measured until the battery voltage reached to a cut-off voltage of 0.9 V.

[0010]

(Example 2)

In the same manner as in Example 1 (including the potential heightening process) except that sulfuric acid aqueous solutions of 10 wt%, 15 wt%, 20 wt% and 30 wt% were used in place of the 5 wt% sulfuric acid aqueous solution, electrolytic manganese dioxides b, c, d and e, and positive electrode mixtures B, C, D and E were produced. Then,

alkaline batteries B, C, D and E were assembled to measure electrode potential and discharge duration of the electrolytic manganese dioxides.

[0011]

(Comparative Example 1)

Electrolytic manganese dioxide for alkaline batteries HH-PF manufactured by Tosoh Corporation, nickel oxyhydroxide and graphite were mixed in a weight ratio of 50:50:5 to prepare a positive electrode mixture f in the same manner as in Example 1. Then, using the positive electrode mixture, an alkaline battery F was assembled and discharge duration thereof was measured in the same manner as in Example 1.

[0012]

(Example 3)

Electrolytic manganese dioxide for alkaline batteries HH-TF manufactured by Tosoh Corporation ( $\text{MnO}_2$  purity: 91% or higher, average particle size obtained by a micro-track method: about 40  $\mu\text{m}$ , pH (JIS): 3.0-4.0, electrode potential:  $275 \pm 15$  mV (vs.  $\text{Hg/HgO}$  (40 wt%  $\text{KOH}$ )), nickel oxyhydroxide and graphite were mixed in a weight ratio of 50:50:5 to prepare a positive electrode mixture g in the same manner as in Example 1 (including the potential heightening process). Then, using the positive electrode mixture, an alkaline battery G was assembled and discharge duration thereof was measured in the same manner as in Example 1. Table 1 shows electrode potentials of the electrolytic manganese dioxides and

discharge durations of the batteries A to G. It is noted that each discharge duration is an average value of 10 batteries, which is expressed with respect to the discharge duration at the initial stage of the battery F regarded as 100.

[0013]

[Table 1]

	Battery No.	Sulfuric acid concentration (wt%)	Electrode potential of manganese dioxide (mV)	Discharge duration (ratio)		Retention ratio after storage (B/A) × 100
				Initial stage(A)	After storage(B)	
Example 1	A	5	272	102	74	73
Example 2	B	10	281	103	77	75
	C	15	288	102	81	79
	D	20	297	100	81	81
	E	30	312	97	79	81
Example 3	G	5	283	104	82	79
Comparative Example 1	F	5	254	100	71	71

(Cut-off voltage 0.9V)

[0014]

As is clear from Table 1, the batteries A to E, which used manganese dioxide having a potential of 270 mV or higher (vs. Hg/HgO (40 wt% KOH)), had an improved discharge performance after high temperature storage in comparison with the battery F, which used manganese dioxide having a potential of 270 mV or lower (vs. Hg/HgO (40 wt% KOH)). The higher the concentration of the sulfuric acid aqueous solution used for the treatment was, the higher the potential of the resultant

manganese dioxide became and so the retention ratio after storage became. Although the reason is not yet clear, the discharge durations at the initial stage of the batteries A to D were longer than that of the battery F while the discharge duration of the battery E was shorter.

[0015]

Next, the content of nickel oxyhydroxide in the positive electrode mixture was examined.

[0016]

(Comparative Example 2)

Electrolytic manganese dioxide for alkaline batteries HH-PF manufactured by Tosoh Corporation, nickel oxyhydroxide and graphite were mixed in the mixing ratio shown in Table 2 to prepare a positive electrode mixture in the same manner as in Example 1 (including the potential heightening step). Then, batteries No. 1 to 8 were assembled.

[0017]

As to the batteries No. 1 to 8, discharge durations at the initial state and after storage at 60°C for 7 days were measured in the same manner as in Example 1. Table 2 shows the results. It is noted that each discharge duration is an average value of 10 batteries, which is expressed with respect to the discharge duration of the battery No. 1 at the initial stage regarded as 100.

[0018]

[Table 2]

Battery No.	Ratio in positive electrode mixture (weight)			Discharge duration ratio		Retention ratio after storage (B/A) × 100(%)
	Manganese dioxide	Nickel oxyhydroxide	Graphite	Initial stage(A)	After storage(B)	
1	100	0	5	100	92	92
2	95	5	5	102	89	87
3	90	10	5	107	91	85
4	80	20	5	116	94	81
5	50	50	5	138	98	71
6	20	80	5	147	90	61
7	10	90	5	157	83	53
8	0	100	5	161	79	49

(Cut-off voltage 0.9V)

[0019]

(Example 3)

Electrolytic manganese dioxide obtained by immersing in an aqueous solution of 15 wt% sulfuric acid in the same manner as in Example 2, nickel oxyhydroxide and graphite were mixed in the mixing ratio shown in Table 3 to prepare a positive electrode mixture in the same manner as Example 1 (including the potential heightening process). Thereby, batteries No. 9 to 14 were assembled.

[0020]

As to the batteries No. 9 to 14, discharge durations at the initial state and after storage at 60°C for 7 days were measured in the same manner as in Example 1. Table 3 shows the results. It is noted that each discharge duration is an

average value of 10 batteries, which is expressed with respect to the discharge duration of the battery No. 1 at the initial stage regarded as 100.

[0021]

[Table 3]

Battery No.	Ratio in positive electrode mixture (weight)			Discharge duration ratio		Retention ratio after storage (B/A) × 100(%)
	Manganese dioxide	Nickel oxyhydroxide	Graphite	Initial stage(A)	After storage(B)	
9	95	5	5	105	93	89
10	90	10	5	111	101	91
11	80	20	5	120	104	87
12	50	50	5	141	111	79
13	20	80	5	148	101	68
14	10	90	5	156	86	55

(Cut-off voltage 0.9V)

[0022]

(Example 4)

Electrolytic manganese dioxide for alkaline batteries HH-TF manufactured by Tosoh Corporation, nickel oxyhydroxide and graphite were mixed in the mixing ratio shown in Table 4 to prepare a positive electrode mixture in the same manner as in Example 1 (including the potential heightening process). Thereby, batteries No. 15 to 20 were assembled.

[0023]

As to the batteries No. 15 to 20, discharge durations at the initial state and after storage at 60°C for 7 days were

measured in the same manner as in Example 1. Table 4 shows the results. It is noted that each discharge duration is an average value of 10 batteries, which is expressed with respect to the discharge duration of the battery No. 1 at the initial stage regarded as 100.

[0024]

[Table 4]

Battery No.	Ratio in positive electrode mixture (weight)			Discharge duration ratio		Retention ratio after storage (B/A) × 100(%)
	Manganese dioxide	Nickel oxyhydroxide	Graphite	Initial stage(A)	After storage(B)	
15	95	5	5	105	93	89
16	90	10	5	113	104	92
17	80	20	5	124	109	88
18	50	50	5	144	114	79
19	20	80	5	150	105	70
20	10	90	5	157	86	55

(Cut-off voltage 0.9V)

[0025]

As is clear from Tables 2 to 4, regardless of the content of nickel oxyhydroxide, the batteries No. 9 to 20 comprising manganese dioxide obtained by immersing in the sulfuric acid aqueous solution or electrolytic manganese dioxide for alkaline batteries HH-TF manufactured by Tosoh Corporation, both of which having a potential of 270 mV or higher (vs. Hg/HgO (40 wt% KOH)), improved in discharge performances after high temperature storage in comparison with



the batteries No. 1 to 8 comprising electrolytic manganese dioxide for alkaline batteries HH-PF manufactured by Tosoh Corporation having a potential of 270 mV or lower (vs. Hg/HgO (40 wt% KOH)). In particular, the improvements in storage characteristics were remarkable when the content of manganese dioxide was 20-90 wt% and the content of nickel oxyhydroxide was 10-80 wt%.

[0026]

In Examples of the present invention, as the potential heightening process, "the slurry was stirred at 60°C for one hour, and thereafter, manganese dioxide was filtered out, washed with water, neutralized with a potassium hydroxide aqueous solution and then washed with water again." However, other methods than the above may be employed as long as electrolytic manganese dioxide is heightened in potential.

[0027]

[Effects of the Invention]

According to the present invention, it is possible to suppress self-discharge reaction of an alkaline battery containing manganese dioxide and nickel oxyhydroxide in a positive electrode mixture and to retain heavy load discharge performance of the alkaline battery even after storage.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1] A front view of an alkaline battery according to an embodiment of the present invention, partially in section.

[Explanation of Reference Numerals]

- 1 Positive electrode case
- 2 Graphite coating film
- 3 Positive electrode mixture pellet
- 4 Separator
- 5 Insulating cap
- 6 Gelled negative electrode
- 7 Resin sealing plate
- 8 Bottom plate
- 9 Insulating washer
- 10 Negative electrode current collector
- 11 Jacket label

2002-030515

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

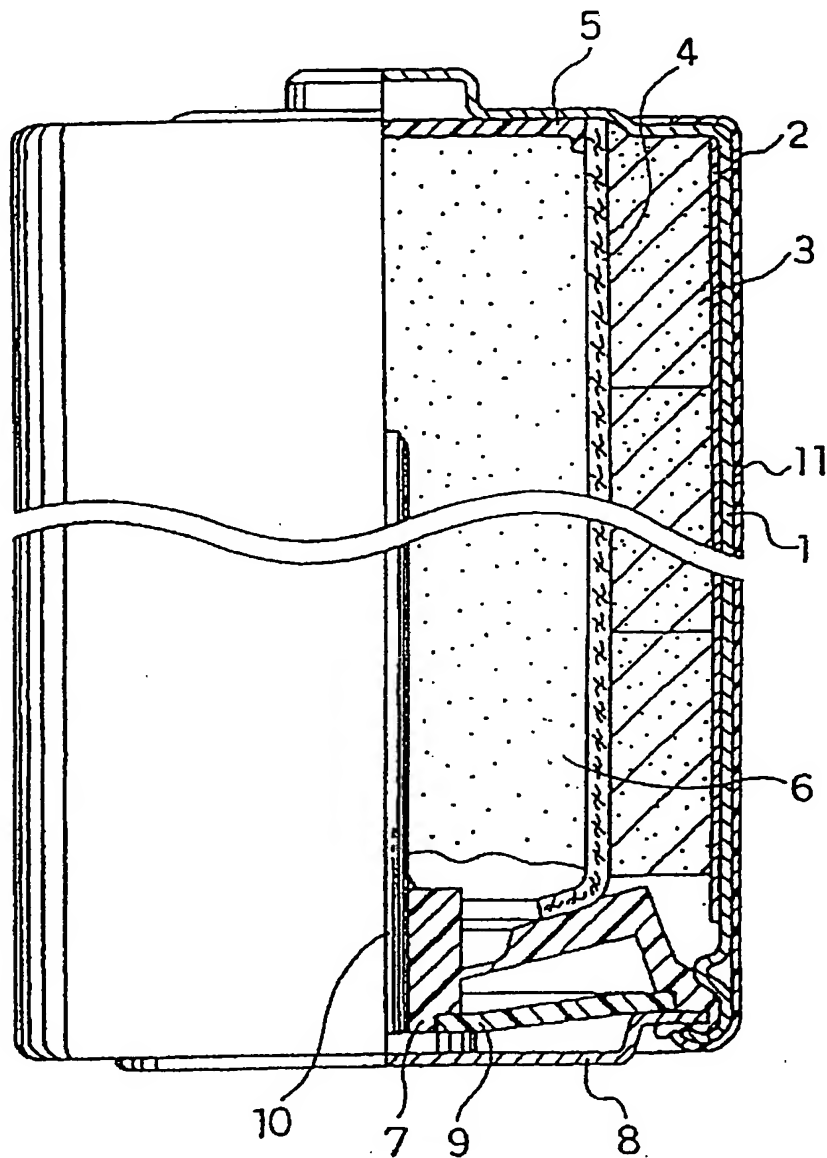
[OBJECTIVE] In view of improvement in an alkaline battery using manganese dioxide and nickel oxyhydroxide as positive electrode active materials, an alkaline battery capable of retaining heavy load discharge performance even after long-term storage at high temperature is provided.

[SOLVING MEANS] An alkaline battery comprising a positive electrode mixture comprising manganese dioxide and nickel oxyhydroxide as active materials, a negative electrode comprising zinc as an active material, and an alkaline electrolyte, in which the potential of the manganese dioxide is 270 mV or higher (vs. Hg/HgO (40 wt% KOH)).

[SELECTED DRAWING] FIG. 1

【書類名】 図面 【DOCUMENT NAME】 Drawings.

【図1】 【FIG. 1】



- |         |            |
|---------|------------|
| 1 正極ケース | 3 正極合剤ペレット |
| 2 黒鉛塗装膜 | 6 ゲル状負極    |

1 Positive electrode case	3 Positive electrode mixture pellet
2 Graphite coating film	6 Gelled negative electrode